Structure and High-Temperature Decomposition Process of LiNiO_2

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1 INTRODUCTION

The layered nickel oxides LiNiO_2 have been studied for possible use as insertion electrodes in 4V rechargeable lithium batteries¹⁻³⁾. In LiNiO_2 , alternate layers of Li and Ni occupy the octahedral sites of a cubic close packing of oxide ions, making up a rhombohedral structure with a $R\bar{3}m$ space group, Li in 3a, Ni in 3b and O in 6c sites. This compound shows structural and compositional varieties depending on their synthesis conditions. The stoichiometric LiNiO_2 is difficult to obtain, because the high-temperature treatment of LiNiO_2 leads to a decomposition from LiNiO_2 to $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ which has a partially disordered cation distribution at the Li site^{4,5)}. The stoichiometry of LiNiO_2 affects the physical properties; the non-stoichiometry led to a significant degradation on the charge and discharge characteristics⁶⁾ and the magnetic properties were extremely sensitive for its cation distribution^{7,8)}. In the present study, we examined precisely the decomposition process from LiNiO_2 to $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ at high temperatures. We synthesized " LiNiO_2 " which is very close to the stoichiometric composition; its structure was determined by the neutron diffraction measurement.

2 EXPERIMENTAL

The ternary oxide LiNiO_2 was prepared by heating an appropriate molar ratios of Li_2O_2 and NiO (Li_2O_2 : Alfa Ltd., >95.3% purity; NiO: Nakarai tesk, >99.9% purity). They were mixed, pelletized in an argon filled glove-box, and then heated in the range of 450 – 850°C under oxygen gas flow. X-Ray diffraction patterns of the powdered samples were obtained with an X-ray diffractometer (Rigaku RAD-C) with $\text{CuK}\alpha$ radiation. The lattice parameters were refined by Rietveld analysis using the computer program RIETAN⁹⁾. Neutron diffraction data were taken on a TOF neutron powder diffractometer, HRP¹⁰⁾, at the KENS pulsed spallation neutron source at the National Laboratory for High Energy Physics (KEK). The electrochemical tests were carried out using lithium cells with 2016 coin-type configuration. Typical electrolytes used were 1 M solutions of LiClO_4 in a 50:50 mixture of propylene carbonate(PC) and 1,2-dimethoxyethane (DME) (Mitsubishi petrochemical company Ltd., battery grade) by volume. The reaction and weight loss of the lithium

nickel oxides on heating up to 1000°C were measured by an automatic differential thermal analysis–thermogravimetry (DTA–TG) apparatus of Rigaku TAS-100.

3 RESULTS AND DISCUSSION

We synthesized the samples according to the method of Thomas et al.¹⁾. The reactions in an oxygen gas flow at 650 – 850°C for 48 h gave the rhombohedral LiNiO_2 ; only a mixture of $\text{Li}_2\text{NiO}_{3-y}$ ¹¹⁾ and NiO was obtained below 500°C. The lattice parameters of the reaction products after the X-ray Rietveld refinement increase slightly from $a = 2.87584(6)$ and $c = 14.1905(4)\text{\AA}$ at 650°C to $a = 2.87899(5)$ and $c = 14.1922(4)\text{\AA}$ at 850°C. The increase in the lattice parameters with reaction temperature indicates a decomposition of LiNiO_2 to $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ at higher temperatures²⁾. The compositions determined by atomic absorption spectroscopy were $\text{Li}_{0.99}\text{Ni}_{1.01}\text{O}_2$ ($\text{Ni}^{2.98+}$), $\text{Li}_{1.00}\text{Ni}_{1.00}\text{O}_2$ ($\text{Ni}^{3.00+}$), and $\text{Li}_{0.93}\text{Ni}_{1.07}\text{O}_2$ ($\text{Ni}^{2.87+}$) for the samples synthesized at 650, 700 and 850°C, respectively.

Neutron diffraction data were obtained for the sample synthesized at 700°C in an oxygen gas flow. The structure was refined with space group $R\bar{3}m$ with the structural model, Li at 3a (0, 0, 0), Ni at 3b (0, 0, 1/2), O at 6c (0, 0, z) with $z \approx 0.25$. The partial disordering of Li and Ni at the Li(3a) and Ni(3b) sites was considered with a constraint that the total occupancy at each site is unity. Table I lists final R factors, lattice and structural parameters, and their estimated standard deviations. The best fit between observed and calculated data in LiNiO_2 synthesized at 700°C yielded the $\alpha\text{-NaFeO}_2$ structure in which the 3a and 3b octahedral sites were mainly occupied by lithium and nickel ions, respectively. The interstitial tetrahedral site Ni(3) at a position (0, 0, $\sim 1/8$) is situated in the NiO_6 octahedral layers. Attempts to refine the occupancy of this site led to an insignificant site occupancy of 0.002(2). Finally, the refined composition $\text{Li}_{0.996}\text{Ni}_{1.006}\text{O}_2$ is in excellent agreement with the expected LiNiO_2 stoichiometry.

The reversibility of the lithium cell, Li/LiNiO_2 , was examined using " LiNiO_2 " prepared at 650, 700 and 850°C. The current density was 0.75 mA/cm² and the cut-off voltages were 2.5 V for discharge and 4.3 V for charge, respectively. A specific capacity of about 150 mAh/g was obtained for the cells with the cathodes prepared at 650 and 700°C. However, a lower capacity of about 130 mAh/g was observed for the cathode prepared at 850°C. The cation disordering on the octahedral sites

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Table I Structural Parameters for LiNiO_2 in $R\bar{3}m$ ($T=300\text{ K}$)

$a=2.87799(8)\text{\AA}$, $c=14.1953(3)\text{\AA}$						
$(R_w=3.65\%$, $R_p=2.82\%$, $R_1=2.64\%$, $R_F=1.65\%$, $S=R_w/R_p=1.17$)						
Atom	Site	g	x	y	z	$B/\text{\AA}^2$
Li	3a	0.996(5)	0	0	0	1.6(2)
Ni(1)	3a	0.004	0	0	0	1.6
Ni(2)	3b	1.0	0	0	1/2	0.31(2)
Ni(3)	6c	0.002(2)	0	0	0.131	0.31
O	6c	1.0	0	0	0.24111(16)	0.86 ^{a)}
Atom	$U_{11}/\text{\AA}^2$	$U_{22}/\text{\AA}^2$	$U_{33}/\text{\AA}^2$	$U_{12}/\text{\AA}^2$	$U_{13}/\text{\AA}^2$	$U_{23}/\text{\AA}^2$
O	0.0110(6)	$=U_{11}$	0.0070(6)	$=U_{11}/2$	0	0

a) Equivalent isotropic thermal parameters, B_{eq} .

affects the reversibility as indicated by the previous studies^{5,6}.

The TG curve in an oxygen gas flow showed a slight weight gain around 800°C , and then showed a large decrease in weight around 920°C accompanied by an endothermic DTA peak. The X-ray diffraction pattern of the sample after the DTA-TG measurement was indexed by a cubic cell of $a = 4.1231(15)\text{\AA}$, indicating a decomposition of LiNiO_2 to $\text{Li}_x\text{Ni}_{1-x}\text{O}$. The decomposition temperature shifts from 920°C in O_2 atmosphere to 750°C in Ar atmosphere, indicating that the decomposition from LiNiO_2 to $\text{Li}_x\text{Ni}_{1-x}\text{O}_2$ was suppressed with increasing oxygen partial pressure in the measurement atmosphere.

To understand the reaction mechanism at higher temperatures, we examined the decomposition process by annealing samples in air or in an oxygen gas flow at various temperatures. The samples synthesized at 850°C were annealed at 300 , 450 , 600 , 700 , 850 , and 1000°C in air or in an oxygen gas flow and then quenched into liq. N_2 . The structural parameters of these samples were refined using the structural models as follows: the cubic $\text{Li}_x\text{Ni}_{1-x}\text{O}$ with disordering cation distribution (space group $\text{Fm}\bar{3}m$) for the 1000°C sample; the rhombohedral $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ with partial disordering at the Li site (space group $R\bar{3}m$) for the samples below 700°C ; a mixture of the cubic $\text{Fm}\bar{3}m$ and the rhombohedral $R\bar{3}m$ phases for the 850°C sample. Figure 1 shows the annealing temperature dependence of the lattice parameters for " LiNiO_2 ". The lattice parameters of the rhombohedral $R\bar{3}m$ phase increase with annealing temperature from 600 to 850°C in air. The rhombohedral phase decomposed to the cubic $\text{Fm}\bar{3}m$ phase above 850°C . The lithium occupancy rate at the Li site, shown in Fig. 1, also decreases with annealing temperature. On the other hand, only a slight increase in the rhombohedral (hexagonal) lattice parameters and no decomposition to the cubic phase were observed for the samples annealed below 850°C in an oxygen gas flow, being consistent with our TG results that the decomposition temperature shifted to higher temperatures with increasing partial oxygen

Fig. 1 (a) Annealing temperature dependence of the lithium occupancy rate in the Li site, and Li/Ni ratio; g values for the samples annealed in O_2 (Δ) and in air ($\circ$); Li/Ni ratios for the sample annealed in O_2 (Δ) and in air ($\bullet$). S.C. indicates the samples cooled slowly from 850°C in O_2 atmosphere. (b) Annealing temperature dependence of the lattice parameters in LiNiO_2 .

pressure in the measurement atmosphere. The oxidizing condition suppressed the decomposition of LiNiO_2 and the reduction from Ni^{3+} to Ni^{2+} state.

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